Question

The reaction scheme $A \underset{k_{21}}{\overset{k^{12}}{\rightleftharpoons}} B \underset{k_{32}}{\overset{k^{23}}{\rightleftharpoons}} C$ is described by the rate equations:

$$\begin{aligned}\frac{dA}{dt} &= -k_{12}A + k_{21}B \\ \frac{dB}{dt} &= k_{12} - (k_{21}+k_{23})B + k_{32}C \\ \frac{dC}{dt} &= k_{23}B - k_{32}C\end{aligned}$$

Solve these equations when $k_{12} = k_{23} = k_{32} = 1, k_{21} = 2$ and

(i) $A(0) = p, B(0) = C(0) = 0$;

(ii) $B(0) = p, A(0) = C(0) = 0$.

What is the equilibrium concentrations in each case?

Answer

In matrix form the equations become: $\begin{pmatrix} \frac{dA}{dt} \\ \frac{dB}{dt} \\ \frac{dC}{dt} \end{pmatrix} = \begin{pmatrix} -1 & 2 & 0 \\ 1 & -3 & 1 \\ 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix}$

$$\begin{aligned}\begin{vmatrix} -1-\lambda & 2 & 0 \\ 1 & -3-\lambda & 1 \\ 0 & 1 & -1-\lambda \end{vmatrix} &= -(1+\lambda)\begin{vmatrix} -3-\lambda & 1 \\ 1 & -1-\lambda \end{vmatrix} - 2\begin{vmatrix} 1 & 1 \\ 0 & -1-\lambda \end{vmatrix} + 0 \\ &= (-1-\lambda)[(1+\lambda)(3+\lambda)-1] + 2(1+\lambda) \\ &= -\lambda(1+\lambda)(\lambda+4) = 0 \\ \text{so } \lambda &= 0, -1, -4\end{aligned}$$

$\underline{\lambda = 0}$ Solve $\begin{pmatrix} -1 & 2 & 0 \\ 1 & -3 & 1 \\ 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$

$$\text{or } \left.\begin{aligned} -x + 2y &= 0 \\ x - 3y + z &= 0 \\ y - z &= 0 \end{aligned}\right\} \quad \begin{aligned} \text{let } y &= \alpha \\ \text{so } x &= 2\alpha \\ z &= \alpha \end{aligned}$$

Suitable eigenvector $\begin{pmatrix} 2\alpha \\ \alpha \\ \alpha \end{pmatrix}$

$\underline{\lambda = -1}$ Solve $\begin{pmatrix} 0 & 2 & 0 \\ 1 & -2 & 0 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$

$$\left.\begin{array}{rcl} 2y &=& 0 \\ \text{or} \quad x-2y+z &=& 0 \\ y &=& 0 \end{array}\right\} \begin{array}{lrcl} & y &=& 0 \\ \text{let} & x &=& \beta \\ \text{so} & z &=& -\beta \end{array}$$

Suitable eigenvector $\begin{pmatrix} \beta \\ 0 \\ -\beta \end{pmatrix}$

$\underline{\lambda = -4}$ Solve $\begin{pmatrix} 3 & 2 & 0 \\ 1 & 1 & 1 \\ 0 & 1 & 3 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$

$$\left.\begin{array}{rcl} 3x+2y &=& 0 \\ \text{or} \quad x+y+z &=& 0 \\ y+3z &=& 0 \end{array}\right\} \begin{array}{lrcl} \text{let} & x &=& 2\gamma \\ \text{so} & y &=& -3\gamma \\ & z &=& \gamma \end{array}$$

Suitable eigenvector $\begin{pmatrix} 2\gamma \\ -3\gamma \\ \gamma \end{pmatrix}$

Hence the general solution is

$$\begin{aligned} \begin{pmatrix} A \\ B \\ C \end{pmatrix} &= \alpha \begin{pmatrix} 2 \\ 1 \\ 1 \end{pmatrix} e^{0t} + \beta \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} e^{-t} + \gamma \begin{pmatrix} 2 \\ -3 \\ 1 \end{pmatrix} e^{-t} \\ &= \alpha \begin{pmatrix} 2 \\ 1 \\ 1 \end{pmatrix} + \beta \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} e^{-t} + \gamma \begin{pmatrix} 2 \\ -3 \\ 1 \end{pmatrix} e^{-t} \end{aligned}$$

(i) if A(0) = p and B(0) = C(0) = 0 then

$$\left.\begin{array}{lrcccl} (1) & A(0) &=& p &=& 2\alpha+\beta+2\gamma \\ (2) & B(0) &=& 0 &=& \alpha-3\gamma \\ (3) & C(0) &=& 0 &=& \alpha-\beta+\alpha \end{array}\right\} \begin{array}{l} (2) \Rightarrow \alpha = 3\gamma \quad (*) \\ \text{sub } (*) \text{ into } (3) \ \Rightarrow \beta = 4\gamma \\ \text{sub } (*) \text{ into } (1) \\ \Rightarrow p = 6\gamma + 4\gamma + 2\gamma = 12\gamma \\ \Rightarrow \gamma = \frac{p}{12} \end{array}$$

Hence $\gamma = \frac{p}{12}, \alpha = \frac{3p}{12} = \frac{p}{4}$ and $\beta = \frac{4p}{12} = \frac{p}{3}$. This gives the particular solution $\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \frac{p}{4} \begin{pmatrix} 2 \\ 1 \\ 1 \end{pmatrix} + \frac{p}{3} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} e^{-t} + \frac{p}{12} \begin{pmatrix} 2 \\ -3 \\ 1 \end{pmatrix} e^{-4t}$.

(ii) if B(0) = q and A(0) = C(0) = 0 then

$$\left.\begin{array}{lrcccl} (1) & A(0) &=& 0 &=& 2\alpha+\beta+2\gamma \\ (2) & B(0) &=& q &=& \alpha-3\gamma \\ (3) & C(0) &=& 0 &=& \alpha-\beta+\alpha \end{array}\right\} \begin{array}{l} (1)-(2) \Rightarrow 3\beta = 0 \Rightarrow \beta = 0 \quad (*) \\ \text{sub } (*) \text{ into } (3) \ \Rightarrow \gamma = -\alpha \\ \text{sub into } (2) \\ \Rightarrow \alpha = \frac{q}{4} \\ \Rightarrow \gamma = -\frac{q}{4} \end{array}$$

This give the particular solution $\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \frac{q}{4}\left[\begin{pmatrix} 2 \\ 1 \\ 1 \end{pmatrix} - \begin{pmatrix} 2 \\ -3 \\ 1 \end{pmatrix} e^{-4t}\right].$

Note:$\lim_{t\to\infty} e^{-t} = 0$ and $\lim_{t\to\infty} e^{-4t} = 0$ Hence as t increases, the exponential part of each solution "dies away". The equilibrium concentration is the limit of the concentration taken as $t \to \infty$.

Cases(i) Equilibrium concentration $\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \frac{p}{4}\begin{pmatrix} 2 \\ 1 \\ 1 \end{pmatrix}$

Cases(ii) Equilibrium concentration $\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \frac{q}{4}\begin{pmatrix} 2 \\ 1 \\ 1 \end{pmatrix}$